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EFFECT OF THE CONDITIONS OF HYDROLYSIS OF TETRAETHOXYSILANE ON THE SYNTHESIS OF FORSTERITE

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The sol-gel process for synthesizing forsterite from magnesium acetate and tetraethoxysilane (TEOS) is investigated. The effect of the conditions of hydrolysis of TEOS on the morphology and phase composition of the powders is studied. It is found that a solution of magnesium acetate and TEOS hydrolysate in an acid medium forms a stable sol which transforms into gel. In this case, the yield of forsterite after heat-treatment at 800°C is 97%. Performing hydrolysis in an alkaline medium and combining the hydrolysis and precipitation of magnesium hydroxide makes it possible to obtain a weakly aggregated powder with composition close to monofractional but the synthesis temperature of forsterite increases.

Sol-gel technology is now making it possible to synthesize multicomponent oxide compounds (silicates, spinels) as well as controlling the properties of ceramic powders and materials.

The sol-gel method is successfully used to obtain forsterite powder, which is of interest for use in electronics and laser technology. For example, in [1] forsterite was synthesized from melts of magnesium salts and amorphous silica in the presence of a solution of polyvinyl alcohol. The authors of [2] propose using an alkoxide precursor — magnesium – silicon cellosolvate. Well-crystallized forsterite powders were obtained only after calcination of hydrolysates at 800°C for 2 h. The 20-nm primary crystallites combine to form large and dense aggregates.

Our previous investigations [3] show that magnesium acetate and silicasol — a sol of amorphous silica — are effectively used to synthesize forsterite. However, a temperature 1200°C is required to complete the formation of forsterite. At this temperature dense aggregates of particles up to 20 μm in size are formed. Thus, the problem of obtaining a monofractional forsterite nanopowder was not solved.

According to the published data, it is preferable to use tetraethoxysilane (TEOS) to synthesize silicates, in particular, forsterite. As a rule, the hydrolysis of TEOS is conducted in a water-alcohol medium with different values of the pH. By changing the conditions of hydrolysis it is possible to obtain particles ranging in size from 5 to 100 nm. In addition, the tendency of silica to polymerize will promote the forma-

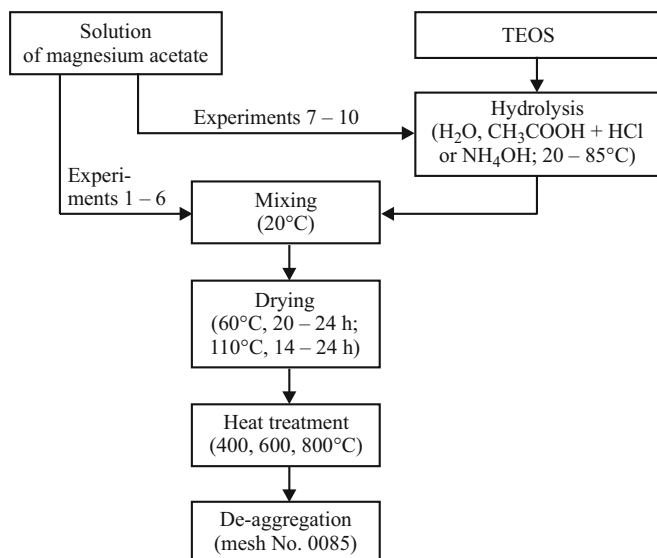tion of Si – O – Mg bonds even at the stage of mixing and hydrolysis.

The main problem of our work is to study the interaction of the products of hydrolysis of TEOS and magnesium acetate in order to obtain a highly disperse forsterite powder with composition close to a single phase and monofractional. To this end, it is proposed that different regimes of TEOS hydrolysis in acidic and alkaline media without organic solvents as well as directly in a solution of magnesium acetate, obtained by dissolving analytically pure magnesium oxide with molar ratio $MgO : H_2O : CH_3COOH = 1.5 : 11.0 : 4.0$, be tested.

The products of the interaction (precursors) were studied by means of IR spectroscopy, XPA, and microscopic analysis. The content of forsterite was determined by quantitative XPA as a function of the ratio of the intensity of the diffraction peaks of the analytical lines of periclase ($d = 2.11$ Å) and forsterite ($d = 2.76$ Å). The precursors and powders were obtained by Scheme 1 presented.

The quantity of reagents was calculated for obtaining forsterite with the stoichiometric composition. The mixing time was chosen for completion of the hydrolysis of TEOS and formation of a uniform sol, which does not separate while standing.

In the experiments 1 – 5 the hydrolysis of TEOS was conducted in an acid medium. The quantitative ratio of TEOS and water was varied from the smallest computed amount 16 : 10 to 16 : 50; the pH was regulated by adding hydrochloric and acetic acids. After hydrolysis was completed, a solution of magnesium acetate was slowly added to the sol obtained and the mixture was mixed with a magnetic mixer for 5 – 10 min.

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┌─────────────────────┐              ┌─────────────────────┐
│     Solution        │              │        TEOS         │
│ of magnesium acetate│              │                     │
└─────────────────────┘              └─────────────────────┘
       │    │                                   │
       │    │  Experiments 7 – 10    ┌───────────────────────────┐
       │    └───────────────────────▶│       Hydrolysis          │
       │                             │ (H₂O, CH₃COOH + HCl        │
 Experi-│                            │ or NH₄OH; 20 – 85°C)       │
 ments 1 – 6                         └───────────────────────────┘
       │         ┌─────────────────┐            │
       └────────▶│    Mixing       │◀───────────┘
                 │    (20°C)       │
                 └─────────────────┘
                          │
                 ┌─────────────────────┐
                 │      Drying         │
                 │ (60°C, 20 – 24 h;   │
                 │  110°C, 14 – 24 h)  │
                 └─────────────────────┘
                          │
                 ┌─────────────────────┐
                 │   Heat treatment    │
                 │ (400, 600, 800°C)   │
                 └─────────────────────┘
                          │
                 ┌─────────────────────┐
                 │   De-aggregation    │
                 │  (mesh No. 0085)    │
                 └─────────────────────┘
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Scheme 1. Obtaining precursors and powders.

TEOS hydrolysate obtained at pH = 2 without heating and with the minimum amount of water (experiment 1) is a transparent sol. Therefore, according to the data of [4], the silica particles do not exceed 7 nm in size. After adding the magnesium acetate solution, the sol remains transparent. Hydrolysis in excess water causes the sol to become cloudy because the particle size increases to 30 nm. Increasing the temperature to 85°C at pH = 3 decreases the hydrolysis time from 50 to 25 min (experiment 3). When the pH is increased to 3.8 (experiment 4) partial gel formation is observed at the TEOS hydrolysis stage; increasing the mixing time to 95 min does not yield a uniform sol.

Preliminary experiments established that heating is required in order to complete TEOS hydrolysis in an alkaline medium. For example, for the volume ratio TEOS : H₂O : NH₄OH = 16 : 40 : 3 hydrolysis is completed at 85°C in 60 min with a cloudy sol being formed. Adding the magnesium acetate solution does not destroy the uniformity of the sol (experiment 6).

As Iler indicates [4], a homogeneous gel is not formed with the hydrolysis of TEOS in the presence of substantial amount of salts at pH > 7. Instead, a white precipitate appears, and in some cases a white opaque gel appears because of the partial precipitation of silica before gel formation occurs. In the present work the hydrolysis of TEOS in the presence of magnesium acetate was conducted in the presence of excess water and without heating (experiments 7 – 9). Hydrolysis is completed in 80 – 120 min with a stable sol being formed. Single-phase sols are probably stable at pH = 5.0 – 5.1 because of the presence of acetate ions.

Two-phase sols containing magnesium hydroxide and silica were also used as precursors. Such sols were obtained by adding an ammonium solution in an amount required for complete precipitation of magnesium hydroxide into acidic hydrolysate of TEOS (experiment 5) or before hydrolysis

(experiment 10). In the latter case the appearance of a bulk precipitate impeded mixing, so that the duration of the hydrolysis was limited to 5 min.

After drying at 60°C for 20 – 24 h the formation of transparent or cloudy gel was observed only in the case where an acidic hydrolysate of TEOS was used. After drying at 110°C glass-like aggregates (experiment 3) or dense, strongly aggregated powders (experiments 1, 2, 4) were obtained. Microscopic analysis showed that such powders have a nonuniform composition and are represented by two types of aggregates: dense "fragment" ranging in size from 8 to 20 μm and shapeless loose aggregates consisting of particles less than 1 μm in size.

Drying the sols obtained on the basis of TEOS hydrolysate in an alkaline medium or in the presence of magnesium acetate results in the formation of loose weakly aggregated powders. Such powders characteristically have a more uniform composition — particles smaller than 1 μm form loose aggregates 5 – 8 μm in size. Aggregates with prismatic shape and size up to 30 μm, probably formed by brucite particles, are present in powder obtained after a two-phase opaque sol is dried (experiment 5).

After heat-treatment at 400 – 800°C the powders obtained on the basis of acidic hydrolysate of TEOS (experiments 1 – 5, 7) are grey and strongly aggregated, and they can be ground only with difficulty. The powders obtained on the basis of alkaline hydrolysate are white and soft, and they can be easily passed through No. 0085 sieve. According to microscopic analysis, when the synthesis temperature is increased from 400 to 800°C aggregates of round particles 3 – 5 μm in size are formed and small particles segregate on the surface of dense glassy aggregates.

Phase transformations at different stages of heat-treatment of the precursors were studied by means of IR spectroscopy. The products of hydrolysis of TEOS after drying at 110°C were analyzed first. The main absorption bands (AB) correspond to vibrations of the Si – O – Si bonds in quartz glass [5]. The absence of AB corresponding to vibrations of Si – O – R (R is an organic radical) bonds attests to the completion of the hydrolysis process. When the hydrolysis medium is changed from acidic to alkaline, the AB of the siloxane bond shift in the direction of high frequencies (1088 – 115 cm^{-1}) as a result of an increase in the degree of condensation.

The effect of the heat-treatment temperature was analyzed for precursors obtained on the basis of the hydrolysate of TEOS in a magnesium acetate solution (Fig. 1). After drying the sol at 110°C, magnesium acetate in the form a crystal hydrate (AB 620, 665, 1027, 1055, and 1439 cm^{-1}) is present in the powder. The wide AB in the range 1440 – 1450 cm^{-1} corresponds to vibrations of molecules of water which is bound with magnesium acetate and silica. Si – O – Si bonds form in the product of hydrolysis of TEOS as a result of a polycondensation reaction (AB 472, 525, and 1106 cm^{-1}). As the temperature increases to 400 – 600°C
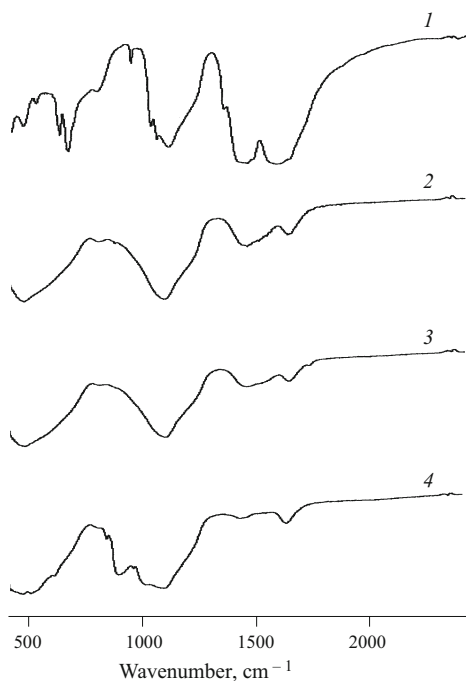
Fig. 1. IR spectra of precursors obtained by hydrolysis of TEOS in a magnesium acetate solution, after heat treatment at 110 (*1*), 400 (*2*), 600 (*3*), and 800°C (*4*).
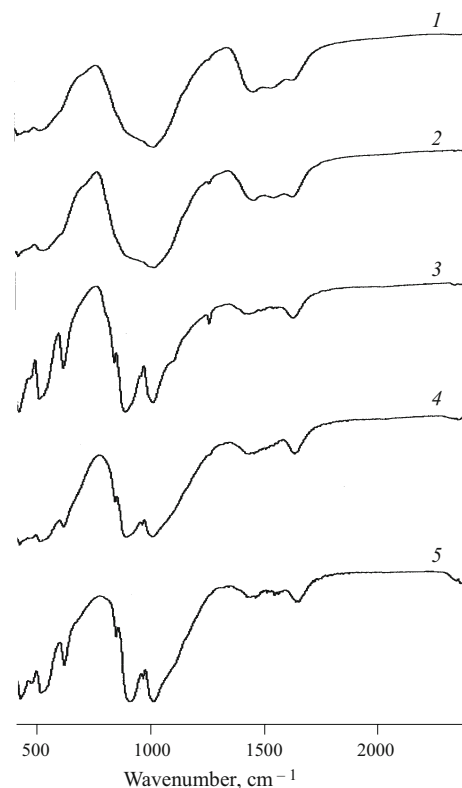

Fig. 2. IR spectra of precursors obtained on the basis of acidic hydrolysate of TEOS, after heat treatment at 400°C (*1*), 600°C (*2*), and 800°C (*3*), as well as precursors obtained on the basis of alkaline hydrolysate of TEOS (*4*), based on the hydrolysate of TEOS and magnesium hydroxide (*5*), after heat treatment at 800°C.

the AB of magnesium acetate vanish and only a small number of wide AB corresponding to the $Si – O – Si$ bonds in amorphous silica remain. After synthesis at 800°C, AB appear at 840 and 960 cm^{-1}. These bands are characteristic for isolated groups $[SiO_4]^{4-}$ and $Si – O – Mg$ bonds in forsterite.

Mg – O and Si – O – Mg bonds, corresponding to the weak AB at 420 cm^{-1} as well as the shoulder at 616 and 950 cm^{-1} (Fig. 2) are formed in the precursor obtained on the basis of acidic hydrolysate of TEOS (experiment 1) already after heat treatment at 400°C. The absorption bands in the interval 1520 – 1650 cm^{-1} correspond to the stretching vibrations of COO$^?$ groups and attest to the formation of acetosiloxane with a small quantity of water. The weak AB at 1265 cm^{-1} can be referred to the C – C bond. As temperature increases to 800°C the AB at 1538 cm^{-1} vanishes, and the intensity of the AB at 1265 cm^{-1} increases, which is explained by the intensification of the C – C bond as clusters of carbon atoms form in aggregates of particles of amorphous silica. Carbon, forming with the decomposition of acetate ions, is probably not removed completely, and becomes bound at the stages of the transition into gel and drying imparts a gray color to the powder.

Only amorphous silica (AB 468 and 1026 cm^{-1}) is present in powders synthesized at 400°C on the basis of alkaline hydrolysate of TEOS. As temperature increases to 600°C, the AB corresponding to $Si – O – Si$ bonds shift slightly to 1037 cm^{-1} as a result of the condensation reaction. $Si – O – Mg$ and $Si – O$ bonds form after heat treatment at 800°C (Fig. 2).

$Si – O$ bonds in isolated $[SiO_4]^{4-}$ form after heat treatment at 600°C in the precursor obtained on the basis of the hydrolysate of TEOS and magnesium hydroxide (experiment 10). After synthesis at 800°C the appearance of AA at 420, 842, and 961 cm^{-1} and the shift of the AB 1026 – 1008 cm^{-1} attest to the appearance of the $Si – O – Mg$ bond, i.e., the onset of the formation of forsterite.

X-ray phase analysis shows that after heat treatment at 800°C the precursors based on acidic hydrolysate of TEOS in experiments 1 – 3 are of a similar character — forsterite and a small quantity of periclase are present. The intensities of the analytical lines of forsterite are virtually identical. According to quantitative analysis, the forsterite content is 90.7 – 97.0% (see Table 1). Hydrolysis at pH = 3.8 in experiment 4 results in an appreciable decrease of the amount of forsterite.

The phase composition was determined for the precursor in experiment 1 at different stages of synthesis. The lines of the initial reagents are not present in the diffraction pattern after heat treatment at 400°C (Fig. 3). The presence of diffuse maximum (halo) in the interval $2\theta = 20 – 44°$ attests to the formation of amorphous products of interaction, whose composition is close to that of forsterite. Forsterite and periclase lines appear at 600°C. The periclase lines are weak,
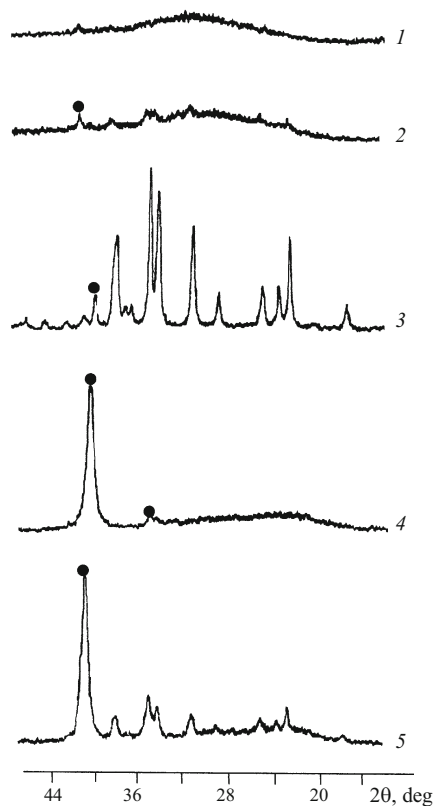
Fig. 3. Diffraction pattern of powders obtained on the basis of acidic hydrolysate of TEOS after heat treatment at 400°C (*1*), 600°C (*2*), and 800°C (*3*) as well as on the basis of alkaline hydrolysate of TEOS after heat treatment at 600°C (*4*) and 800°C (*5*): ●) periclase; no labeling) forsterite.

indicating that magnesium ions are bound by the products of hydrolysis of TEOS at the early stages of obtaining the precursor. The synthesis of forsterite is virtually complete after heat treatment at 800°C.

The precipitation of magnesium hydroxide after the completion of the hydrolysis of TEOS in an acidic medium (experiment 5) results in, after synthesis at 800°C, a decrease of the amount of forsterite and in the appearance of enstatite. Evidently, this is due to the disruption of the uniformity as a result of the formation of large periclase crystals. In powders obtained on the basis of alkaline hydrolysate of TEOS in experiment 6, only periclase and an amorphous phase are present after heat treatment at 600°C. After heat treatment at 800°C the periclase lines in the diffraction pattern become weaker and forsterite lines appear, which attests to the crystallization of forsterite.

Hydrolysis in a solution of magnesium acetate at pH = 5.0 – 5.1 (experiments 7 – 9) appreciable decreases the intensity of the forsterite lines. Only periclase and an amorphous phase are present in powders synthesized at 400 – 600°C. A small amount of forsterite forms after synthesis at 800°C. In experiment 10, the combination of precipitation of magnesium hydroxide and hydrolysis of TEOS promotes synthesis of forsterite, whose amount at 800°C is 82.2%.

In summary, the use of magnesium acetate and hydrolysate of EOS in an acidic medium with pH = 2 with no heating and with the minimum amount of water permits completion of forsterite formation at 800°C. Drying and heat treatment are accompanied by aggregation of particles and disruption of the uniformity of the granulometric composi-

TABLE 1.

Experiment	Synthesis temperature, °C	Phase composition	I_f^*, arb. units	I_p/I_f^*	Forsterite amount, %
1	400	Amorphous phase	–	–	–
	600	Forsterite, periclase, amorphous phase	6	1.21	71.6
	800	Forsterite, periclase	42	0.10	97.0
2	800	Same	44	0.33	90.7
3	800	"	45	0.28	< 70.0
4	800	Periclase, forsterite, amorphous phase	33	2.06	< 70.0
5	800	Periclase, forsterite, amorphous phase, enstatite	14	4.70	< 70.0
6	600	Periclase, amorphous phase	–	–	–
	800	Periclase, forsterite, amorphous phase	26	1.61	< 70.0
7	800	Same	10	–	Not determined
8	800	"	4	–	Same
9	400	Periclase, amorphous phase	–	–	–
	600	Same	–	–	–
	800	Periclase, forsterite, amorphous phase	9	7.68	< 70.0
10	600	Same	7	4.11	< 70.0
	800	"	27	0.72	82.2

* I_f) intensity of the analytical line of forsterite.

** I_p/I_f) ratio of the intensities of lines of periclase and forsterite.

tion. In the future, it is necessary to choose conditions for effective de-aggregation of the powders. Hydrolysis of TEOS in an alkaline medium yields powder with close to monofractional composition but increases the temperature of synthesis of forsterite.

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